

CERTIFICATION

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Tokyo 105-0001, Japan, hereby certify that the following is a true and  
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【 DESIGNATION OF THE DOCUMENT 】 SPECIFICATION  
【 TITLE OF THE INVENTION 】 FOAMED LAMINATE  
BASED ON OLEFIN

【 PATENT CLAIMS 】

【 CLAIM 1 】 A foamed laminate based on olefin  
in which

a substrate layer, consisting of a foamed body ( $X_2$ )  
made of a foamable olefinic composition ( $X_1$ ) comprising  
100 parts by weight of an olefinic thermoplastic  
elastomer (A), 1 - 20 parts by weight of an olefinic  
thermoplastic resin (B) and a foaming agent (C), and

a skin layer made of an ultrahigh molecular weight  
polyolefin resin (Y),

are laminated,

wherein the said olefinic thermoplastic elastomer (A)  
is one which is obtained by subjecting a mixture  
comprising 5 - 60 parts by weight of a polyolefin resin  
(a-1) and 40 - 95 parts by weight of an ethylene/ $\alpha$ -olefin  
copolymer rubber (a-2) resulting from copolymerization  
of ethylene, an  $\alpha$ -olefin and, optionally incorporated, a  
non-conjugated polyene, with the said constituents (a-1)  
and (a-2) summing up to 100 parts by weight, to a  
dynamic heat treatment,

the said olefinic thermoplastic resin (B) is one which  
has an olefin content of 50 - 100 mole % and a melt flow  
rate (ASTM D-1238-65T, 230 °C, 2.16 kg load) of 0.01 -  
2 g/10 min. and

the said ultrahigh molecular weight polyolefin resin  
(Y) is one which has an intrinsic viscosity ( $\eta$ ) of 3.5 -  
8.3 dl/g determined in decalin at 135 °C.

【 CLAIM 2 】      A foamed laminate based on olefin in which

a substrate layer, consisting of a foamed body ( $X_2$ ) made of a foamable olefinic composition ( $X_1$ ) comprising 100 parts by weight of an olefinic thermoplastic elastomer (A), 1 - 20 parts by weight of an olefinic thermoplastic resin (B) and a foaming agent (C), and

a skin layer made of an olefinic thermoplastic elastomer composition ( $Z_1$ )

are laminated,

wherein the said olefinic thermoplastic elastomer (A) is one which is obtained by subjecting a mixture comprising 5 - 60 parts by weight of a polyolefin resin (a-1) and 40 - 95 parts by weight of an ethylene/ $\alpha$ -olefin copolymer rubber (a-2) resulting from copolymerization of ethylene, an  $\alpha$ -olefin and, optionally incorporated, a non-conjugated polyene, with the said constituents (a-1) and (a-2) summing up to 100 parts by weight, to a dynamic heat treatment,

the said olefinic thermoplastic resin (B) is one which has an olefin content of 50 - 100 mole % and a melt flow rate (ASTM D-1238-65T, 230 °C, 2.16 kg load) of 0.01 - 2 g/10 min. and

the said olefinic thermoplastic elastomer composition ( $Z_1$ ) is one which comprises, per 100 parts by weight of an olefinic thermoplastic elastomer component (D), at least one kind selected from the group consisting of 0.5 - 25 parts by weight of an organopolysiloxane (E), 0.5 - 10 parts by weight of a fluorine-containing polymer (F) and 0.5 - 10 parts by weight of an antistatic agent (G), each

in a proportion as given above.

【 CLAIM 3 】 A foamed laminate based on olefin in which

a substrate layer, consisting of a foamed body ( $X_2$ ) made of a foamable olefinic composition ( $X_1$ ) comprising 100 parts by weight of an olefinic thermoplastic elastomer (A), 1 - 20 parts by weight of an olefinic thermoplastic resin (B) and a foaming agent (C), and

a skin layer made of an olefinic thermoplastic elastomer composition ( $Z_2$ )

are laminated,

wherein the said olefinic thermoplastic elastomer (A) is one which is obtained by subjecting a mixture comprising 5 - 60 parts by weight of a polyolefin resin (a-1) and 40 - 95 parts by weight of an ethylene/ $\alpha$ -olefin copolymer rubber (a-2) resulting from copolymerization of ethylene, an  $\alpha$ -olefin and, optionally incorporated, a non-conjugated polyene, with the said constituents (a-1) and (a-2) summing up to 100 parts by weight, to a dynamic heat treatment,

the said olefinic thermoplastic resin (B) is one which has an olefin content of 50 - 100 mole % and a melt flow rate (ASTM D-1238-65T, 230 °C, 2.16 kg load) of 0.01 - 2 g/10 min. and

the said olefinic thermoplastic elastomer composition ( $Z_2$ ) is one which comprises, per 100 parts by weight of an olefinic thermoplastic elastomer (D), a polyolefin resin (H) in an amount of 5 - 200 parts by weight.

【 CLAIM 4 】 A foamed laminate based on olefin in which

a substrate layer, consisting of a foamed body ( $X_2$ ) made of a foamable olefinic composition ( $X_1$ ) comprising 100 parts by weight of an olefinic thermoplastic elastomer (A), 1 - 20 parts by weight of an olefinic thermoplastic resin (B) and a foaming agent (C), and

a skin layer made of an olefinic thermoplastic elastomer composition ( $Z_3$ )

are laminated,

wherein the said olefinic thermoplastic elastomer (A) is one which is obtained by subjecting a mixture comprising 5 - 60 parts by weight of a polyolefin resin (a-1) and 40 - 95 parts by weight of an ethylene/ $\alpha$ -olefin copolymer rubber (a-2) resulting from copolymerization of ethylene, an  $\alpha$ -olefin and, optionally incorporated, a non-conjugated polyene, with the said constituents (a-1) and (a-2) summing up to 100 parts by weight, to a dynamic heat treatment,

the said olefinic thermoplastic resin (B) is one which has an olefin content of 50 - 100 mole % and a melt flow rate (ASTM D-1238-65T, 230 °C, 2.16 kg load) of 0.01 - 2 g/10 min. and

wherein the said olefinic thermoplastic elastomer composition ( $Z_3$ ) is one which comprises, per 100 parts by weight of an olefinic thermoplastic elastomer (D), at least one kind selected from the group consisting of 0.5 - 25 parts by weight of an organopolysiloxane (E), 0.5 - 10 parts by weight of a fluorine-containing polymer (F) and 0.5 - 10 parts by weight of an antistatic agent (G), each in a proportion given above, and further comprises a polyolefin resin (H) in an amount of 5 - 200 parts by



weight.

【 CLAIM 5 】 The foamed laminate based on olefin, as claimed in any one of claims 2 to 4, wherein the olefinic thermoplastic elastomer (D) is one which is obtained by a dynamic heat treatment of a mixture comprising a crystalline polyolefin resin (d-1) and a rubber (d-2).

【 CLAIM 6 】 The foamed laminate based on olefin, as claimed in claim 3 or 4, wherein the polyolefin resin (H) is an ultrahigh molecular weight polyolefin resin (Y).

【 CLAIM 7 】 The formed laminate based on olefin, as claimed in claim 1, 3, 4 or 6, wherein the ultrahigh molecular weight polyolefin resin (Y) comprises 15 - 40 parts by weight of an ultrahigh molecular weight polyolefin resin (y-1) having an intrinsic viscosity ( $\eta$ ) of 10 - 40 dl/g as determined in decalin at 135 °C and 85 - 60 parts by weight of a polyolefin resin (y-2) having an intrinsic viscosity ( $\eta$ ) of 0.1 - 5 dl/g as determined in decalin at 135 °C, with the said constituents (y-1) and (y-2) summing up to 100 parts by weight.

【 CLAIM 8 】 The foamed laminate based on olefin, as claimed in any one of claims 1 to 7, wherein the polyolefin resin (a-1) of the olefinic thermoplastic elastomer (A) is a polypropylene resin.

【 CLAIM 9 】 The foamed laminate based on olefin, as claimed in any one of claims 1 to 8, wherein the olefinic thermoplastic elastomer (A) comprises further 10 - 200 parts by weight of a softening agent

(a-3) per 100 parts by weight of the ethylene/ $\alpha$ -olefin copolymer rubber (a-2).

【CLAIM 10】 The foamed laminate based on olefin, as claimed in any one of claims 1 to 9, wherein the olefinic thermoplastic elastomer (A) is a thermoplastic elastomer composition obtained by subjecting a mixture comprising the polyolefin resin (a-1) and the ethylene/ $\alpha$ -olefin copolymer rubber (a-2) or a mixture which comprises further, optionally incorporated, the softening agent (a-3) to a dynamic heat treatment in the presence of a cross-linking agent.

【CLAIM 11】 The foamed laminate based on olefin, as claimed in any one of claims 1 to 10, wherein the olefinic thermoplastic resin (B) is an isotactic polypropylene or a propylene/ $\alpha$ -olefin copolymer.

【CLAIM 12】 The foamed laminate based on olefin, as claimed in any one of claims 1 to 11, wherein the foaming agent (C) is an organic or an inorganic foaming agent of heat-decomposition type.

【CLAIM 13】 The foamed laminate based on olefin, as claimed in any one of claims 1 to 12, wherein the content of the foaming agent (C) is in the range of 0.5 - 20 parts by weight per 100 parts by weight of total sum of the olefinic thermoplastic elastomer (A) and the olefinic thermoplastic resin (B).

【CLAIM 14】 The foamed laminate based on olefin, as claimed in any one of claims 1 to 13, wherein the foaming expansion ratio of the foamed body ( $X_2$ ) is at least twofold.

【CLAIM 15】 The foamed laminate based on

olefin, as claimed in any one of claims 2 to 4, wherein the olefinic thermoplastic elastomer (D) is one which is obtained by subjecting a mixture comprising the crystalline polyolefin resin (d-1) and the rubber (d-2) to a dynamic heat treatment in the presence of a cross-linking agent.

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**【 DETAILED DESCRIPTION OF THE INVENTION 】****【 0001 】****【 TECHNICAL FIELD OF THE INVENTION 】**

The present invention relates to a foamed laminate based on olefin, in which an olefinic foamed body is used for the substrate layer and an ultrahigh molecular weight polyolefin resin or an olefinic thermoplastic elastomer composition is used for the skin layer.

**【 0002 】****【 PRIOR ART 】**

As a technique for producing foamed articles of elastomer (vulcanized rubber), a process has hitherto been known, in which a vulcanizing agent and a foaming agent are admixed to natural rubber or a synthetic rubber and kneaded, whereupon the resulting kneaded mass is formed into a contemplated shape, followed by heating to effect vulcanization and foaming to obtain a foamed article of elastomer.

By the above-mentioned prior technique, however, it is necessary for forming the said rubber into a predetermined shape by continuous extrusion to perform preliminarily a process step of kneading a composite blend together with the rubber to obtain the kneaded mass before the continuous extrusion and to carry out thereafter a process step of forming the kneaded mass into a form of ribbon preliminarily for facilitation of easy supply of the kneaded mass to the extruding machine before the continuous kneading. Thus, the prior technique as given above is disadvantageous in the industrial production, since the production process steps

are intricate and, in addition, considerable time is required for both the process steps of vulcanization and of foaming.

【 0003 】

As a technique for solving such problems, there is a method of using, for example, a thermoplastic resin, such as an ethylene/vinyl acetate copolymer, low density polyethylene or so on, or a partially cross-linked thermoplastic elastomer constituted of an olefinic copolymer rubber and an olefinic resin. According to this method, the process steps mentioned above can be dispensed with.

【 0004 】

However, thermoplastic resins and thermoplastic elastomers conventionally used have problems that inferior appearance may be apt to occur due to the tendency to occurrence of defoaming upon the foaming molding and that the foaming expansion ratio of the foamed article is lower, as amounting only to about 1.5 times, whereby a harder hand touch will result.

Further, when a part element subject to repeated sliding or a partial component subject to contact with human or materials, such as weather strip or sealing element on window sash for automobile, is produced from a conventional foamed body, it may difficultly be served for practical use as a sliding element or the like by inferior durability thereof due to the poor resistance to abrasion and lower sliding performance thereof.

【 0005 】

【 SUBJECT TO BE SOLVED BY THE INVENTION 】

An object of the present invention is to solve the problems concomitant with the prior technique mentioned above and to provide a foamed laminate based on olefin which is made of an olefinic polymer premitting recycled use and obtainable at a high foaming expansion ratio and, thus, exhibits a soft hand touch and which is superior in the appearance, in the resistance to abrasion, in the durability and in the sliding performance.

【 0006 】

【 MEANS FOR SOLVING THE SUBJECT 】

The present invention resides in the following foamed laminate based on olefin:

(1) A foamed laminate based on olefin in which

a substrate layer, consisting of a foamed body ( $X_2$ ) made of a foamable olefinic composition ( $X_1$ ) comprising 100 parts by weight of an olefinic thermoplastic elastomer (A), 1 - 20 parts by weight of an olefinic thermoplastic resin (B) and a foaming agent (C), and

a skin layer made of an ultrahigh molecular weight polyolefin resin (Y),

are laminated,

wherein the said olefinic thermoplastic elastomer (A) is one which is obtained by subjecting a mixture comprising 5 - 60 parts by weight of a polyolefin resin (a-1) and 40 - 95 parts by weight of an ethylene/ $\alpha$ -olefin copolymer rubber (a-2) resulting from copolymerization of ethylene, an  $\alpha$ -olefin and, optionally incorporated, a non-conjugated polyene, with the said constituents (a-1) and (a-2) summing up to 100 parts by weight, to a dynamic heat treatment,

the said olefinic thermoplastic resin (B) is one which has an olefin content of 50 - 100 mole % and a melt flow rate (ASTM D-1238-65T, 230 °C, 2.16 kg load) of 0.01 - 2 g/10 min. and

the said ultrahigh molecular weight polyolefin resin (Y) is one which has an intrinsic viscosity ( $\eta$ ) of 3.5 - 8.3 dl/g determined in decalin at 135 °C.

(2) A foamed laminate based on olefin in which

a substrate layer, consisting of a foamed body ( $X_2$ ) made of a foamable olefinic composition ( $X_1$ ) comprising 100 parts by weight of an olefinic thermoplastic elastomer (A), 1 - 20 parts by weight of an olefinic thermoplastic resin (B) and a foaming agent (C), and

a skin layer made of an olefinic thermoplastic elastomer composition ( $Z_1$ )

are laminated,

wherein the said olefinic thermoplastic elastomer (A) is one which is obtained by subjecting a mixture comprising 5 - 60 parts by weight of a polyolefin resin (a-1) and 40 - 95 parts by weight of an ethylene/ $\alpha$ -olefin copolymer rubber (a-2) resulting from copolymerization of ethylene, an  $\alpha$ -olefin and, optionally incorporated, a non-conjugated polyene, with the said constituents (a-1) and (a-2) summing up to 100 parts by weight, to a dynamic heat treatment,

the said olefinic thermoplastic resin (B) is one which has an olefin content of 50 - 100 mole % and a melt flow rate (ASTM D-1238-65T, 230 °C, 2.16 kg load) of 0.01 - 2 g/10 min. and

the said olefinic thermoplastic elastomer composition

(Z<sub>1</sub>) is one which comprises, per 100 parts by weight of an olefinic thermoplastic elastomer component (D), at least one kind selected from the group consisting of 0.5 - 25 parts by weight of an organopolysiloxane (E), 0.5 - 10 parts by weight of a fluorine-containing polymer (F) and 0.5 - 10 parts by weight of an antistatic agent (G), each in a proportion as given above.

(3) A foamed laminate based on olefin in which

a substrate layer, consisting of a foamed body (X<sub>2</sub>) made of a foamable olefinic composition (X<sub>1</sub>) comprising 100 parts by weight of an olefinic thermoplastic elastomer (A), 1 - 20 parts by weight of an olefinic thermoplastic resin (B) and a foaming agent (C), and

a skin layer made of an olefinic thermoplastic elastomer composition (Z<sub>2</sub>)

are laminated,

wherein the said olefinic thermoplastic elastomer (A) is one which is obtained by subjecting a mixture comprising 5 - 60 parts by weight of a polyolefin resin (a-1) and 40 - 95 parts by weight of an ethylene/ $\alpha$ -olefin copolymer rubber (a-2) resulting from copolymerization of ethylene, an  $\alpha$ -olefin and, optionally incorporated, a non-conjugated polyene, with the said constituents (a-1) and (a-2) summing up to 100 parts by weight, to a dynamic heat treatment,

the said olefinic thermoplastic resin (B) is one which has an olefin content of 50 - 100 mole % and a melt flow rate (ASTM D-1238-65T, 230 °C, 2.16 kg load) of 0.01 - 2 g/10 min. and

the said olefinic thermoplastic elastomer composition



(Z<sub>2</sub>) is one which comprises, per 100 parts by weight of an olefinic thermoplastic elastomer (D), a polyolefin resin (H) in an amount of 5 - 200 parts by weight.

(4) A foamed laminate based on olefin in which a substrate layer, consisting of a foamed body (X<sub>2</sub>) made of a foamable olefinic composition (X<sub>1</sub>) comprising 100 parts by weight of an olefinic thermoplastic elastomer (A), 1 - 20 parts by weight of an olefinic thermoplastic resin (B) and a foaming agent (C), and

a skin layer made of an olefinic thermoplastic elastomer composition (Z<sub>3</sub>)

are laminated,

wherein the said olefinic thermoplastic elastomer (A) is one which is obtained by subjecting a mixture comprising 5 - 60 parts by weight of a polyolefin resin (a-1) and 40 - 95 parts by weight of an ethylene/ $\alpha$ -olefin copolymer rubber (a-2) resulting from copolymerization of ethylene, an  $\alpha$ -olefin and, optionally incorporated, a non-conjugated polyene, with the said constituents (a-1) and (a-2) summing up to 100 parts by weight, to a dynamic heat treatment,

the said olefinic thermoplastic resin (B) is one which has an olefin content of 50 - 100 mole % and a melt flow rate (ASTM D-1238-65T, 230 °C, 2.16 kg load) of 0.01 - 2 g/10 min. and

wherein the said olefinic thermoplastic elastomer composition (Z<sub>3</sub>) is one which comprises, per 100 parts by weight of an olefinic thermoplastic elastomer (D), at least one kind selected from the group consisting of 0.5 - 25 parts by weight of an organopolysiloxane (E), 0.5 - 10

parts by weight of a fluorine-containing polymer (F) and 0.5 - 10 parts by weight of an antistatic agent (G), each in a proportion given above, and further comprises a polyolefin resin (H) in an amount of 5 - 200 parts by weight.

(5) The foamed laminate based on olefin, as defined in any one of the above (2) to (4), wherein the olefinic thermoplastic elastomer (D) is one which is obtained by a dynamic heat treatment of a mixture comprising a crystalline polyolefin resin (d-1) and a rubber (d-2).

(6) The foamed laminate based on olefin as defined in the above (3) or (4), wherein the polyolefin resin (H) is an ultrahigh molecular weight polyolefin resin (Y).

(7) The formed laminate based on olefin as defined in the above (1), (3), (4) or (6), wherein the ultrahigh molecular weight polyolefin resin (Y) comprises 15 - 40 parts by weight of an ultrahigh molecular weight polyolefin resin (y-1) having an intrinsic viscosity ( $\eta$ ) of 10 - 40 dl/g as determined in decalin at 135 °C and 85 - 60 parts by weight of a polyolefin resin (y-2) having an intrinsic viscosity ( $\eta$ ) of 0.1 - 5 dl/g as determined in decalin at 135 °C, with the said constituents (y-1) and (y-2) summing up to 100 parts by weight.

(8) The foamed laminate based on olefin, as defined in any one of the above (1) to (7), wherein the polyolefin resin (a-1) of the olefinic thermoplastic elastomer (A) is a polypropylene resin.

(9) The foamed laminate based on olefin, as defined in any one of the above (1) to (8), wherein the olefinic thermoplastic elastomer (A) comprises further 10 - 200

parts by weight of a softening agent (a-3) per 100 parts by weight of the ethylene/ $\alpha$ -olefin copolymer rubber (a-2).

(10) The foamed laminate based on olefin, as defined in any one of the above (1) to (9), wherein the olefinic thermoplastic elastomer (A) is a thermoplastic elastomer composition obtained by subjecting a mixture comprising the polyolefin resin (a-1) and the ethylene/ $\alpha$ -olefin copolymer rubber (a-2) or a mixture which comprises further, optionally incorporated, the softening agent (a-3) to a dynamic heat treatment in the presence of a cross-linking agent.

(11) The foamed laminate based on olefin, as defined in any one of the above (1) to (10), wherein the olefinic thermoplastic resin (B) is an isotactic polypropylene or a propylene/ $\alpha$ -olefin copolymer.

(12) The foamed laminate based on olefin, as defined in any one of the above (1) to (11), wherein the foaming agent (C) is an organic or an inorganic foaming agent of heat-decomposition type.

(13) The foamed laminate based on olefin, as defined in any one of the above (1) to (12), wherein the content of the foaming agent (C) is in the range of 0.5 - 20 parts by weight per 100 parts by weight of total sum of the olefinic thermoplastic elastomer (A) and the olefinic thermoplastic resin (B).

(14) The foamed laminate based on olefin, as defined in any one of the above (1) to (13), wherein the foaming expansion ratio of the foamed body ( $X_2$ ) is at least twofold.

(15) The foamed laminate based on olefin, as defined in any one of the above (2) to (4), wherein the olefinic thermoplastic elastomer (D) is one which is obtained by subjecting a mixture comprising the crystalline polyolefin resin (d-1) and the rubber (d-2) to a dynamic heat treatment in the presence of a cross-linking agent.

【 0007 】

○ The olefinic thermoplastic elastomer (A)

The olefinic thermoplastic elastomer (A) to be used as the raw material of the substrate layer according to the present invention is an olefinic thermoplastic elastomer obtained by dynamically heat-treating a mixture comprising 5 - 60 parts by weight, preferably 10 - 50 parts by weight, of a polyolefin resin (a-1) and 40 - 95 parts by weight, preferably 50 - 90 parts by weight, of an ethylene/ $\alpha$ -olefin copolymer rubber (a-2), with the total of the components (a-1) and (a-2) summing up to 100 parts by weight. The olefinic thermoplastic elastomer (A) may contain, in addition to the components (a-1) and (a-2), further, if necessary, other component(s), such as a softening agent (a-3) and so on.

【 0008 】

The olefinic thermoplastic elastomer (A) to be used according to the present invention may favorably be an olefinic thermoplastic elastomer obtained by subjecting a mixture comprising the polyolefin resin (a-1) and the ethylene/ $\alpha$ -olefin copolymer rubber (a-2) in the above-mentioned proportion and, further, if necessary, a softening agent (a-3) and so on, to a dynamic heat treatment in the presence of a cross-linking agent.

When the contents of the polyolefin resin (a-1) and of the ethylene/ $\alpha$ -olefin copolymer rubber (a-2) are in the above-mentioned ranges, respectively, a foamed body ( $X_2$ ) superior in the flexibility and a foamable olefinic composition ( $X_1$ ) superior in the flowability can be obtained.

【 0009 】

The polyolefin resin (a-1) is a resin constituted of a crystalline high molecular weight solid product obtained by polymerizing one or two or more monoolefins by a high pressure process or a low pressure process. For such a resin, there may be recited, for example, monoolefinic polymer or copolymer resins of isotactic and syndiotactic natures. Typical products of these resins are available in the market.

【 0010 】

As suitable starting olefins of the polyolefin resin (a-1), there may concretely be enumerated, for example,  $\alpha$ -olefins having 2 - 20 carbon atoms, such as ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 1-octene, 1-decene, 2-methyl-1-propene, 3-methyl-1-pentene, 4-methyl-1-pentene and 5-methyl-1-hexene. These olefins may be employed each individually or in a combination of two or more of them.

【 0011 】

As the polyolefin resin (a-1), homopolymers of propylene and copolymers composed mainly of propylene with other olefins are preferable. As the copolymers, concretely, for example, propylene/ethylene copolymer, propylene/1-butene copolymer, propylene/1-hexene

copolymer and propylene/4-methyl-1-pentene copolymer are preferred.

【 0012 】

The polyolefin resin (a-1) may favorably have a melt flow rate (MFR: ASTM D-1238-65T, 230 °C , 2.16 kg load) usually in the range from 0.01 to 100 g/10 min., preferably from 0.05 to 50 g/10 min.

The polyolefin resin (a-1) has a function of improving the flowability of the resin composition and increasing the heat resistance.

The polyolefin resin (a-1) may be used either individually or in a combination of two or more kinds.

【 0013 】

The ethylene/ $\alpha$ -olefin copolymer rubber (a-2) to be used according to the present invention is an ethylene/ $\alpha$ -olefin copolymer rubber and/or an ethylene/ $\alpha$ -olefin/non-conjugated polyene copolymer rubber and is an elastomeric copolymer having amorphous and random structure.

【 0014 】

Concrete examples of the  $\alpha$ -olefin include those having 3 - 20 carbon atoms, such as propylene, 1-butene, 1-pentene, 1-hexene, 1-octene, 1-decene, 2-methyl-1-propene, 3-methyl-1-pentene, 4-methyl-1-pentene and 5-methyl-1-hexene. These olefins may be used each individually or in a mixture of two or more of them.

【 0015 】

As the non-conjugated polyene, there may be enumerated concretely, for example, dicyclopentadiene,

1,4-hexadiene, cyclooctadiene, methylenenorbornene, ethylenenorbornene and vinylnorbornene.

【 0016 】

As the ethylene/ $\alpha$ -olefin copolymer rubber (a-2), for example, an ethylene/propylene copolymer rubber, an ethylene/propylene/non-conjugated polyene copolymer rubber, an ethylene/1-butene copolymer rubber and an ethylene/1-butene/non-conjugated polyene copolymer rubber are preferred. Especially preferable ones are rubbers, in particular, ethylene/propylene/ethylenenorbornene copolymer rubber and ethylene/propylene/dicyclopentadiene copolymer rubber, which are preferable especially in the point of view of that an olefinic thermoplastic elastomer (A) having a proper cross-linked structure can be obtained.

【 0017 】

The ethylene/ $\alpha$ -olefin copolymer rubber (a-2) to be used according to the present invention may favorably have an ethylene content in the range from 55 to 95 mole %, preferably from 60 to 90 mole %.

The ethylene/ $\alpha$ -olefin copolymer rubber (a-2) may favorably have a Mooney viscosity [ $ML_{1+4}(100\text{ }^{\circ}\text{C})$ ] in the range from 10 to 250, preferably from 30 to 160.

The ethylene/ $\alpha$ -olefin copolymer rubber (a-2) may favorably have an iodine value of 25 or lower, preferably in the range from 5 to 25. When the iodine value of the ethylene/ $\alpha$ -olefin copolymer rubber (a-2) is 25 or lower, an olefinic thermoplastic elastomer (A) having a proper

cross-linked structure is obtained.

【 0018 】

The ethylene/ $\alpha$ -olefin copolymer rubber (a-2) may be incorporated either individually or in a combination of two or more kinds.

According to the present invention, it is also possible to incorporate the ethylene/ $\alpha$ -olefin copolymer rubber (a-2) in combination with other rubber(s) other than the ethylene/ $\alpha$ -olefin copolymer rubber (a-2), within the range not obstructing the purpose of the present invention.

【 0019 】

As the rubbers other than the ethylene/ $\alpha$ -olefin copolymer rubber (a-2), there may be recited, for example, a propylene/ $\alpha$ -olefin copolymer rubber (with a propylene/ $\alpha$ -olefin mole ratio in the range from 90/10 to 50/50), a butene/ $\alpha$ -olefin copolymer rubber (with a butene/ $\alpha$ -olefin mole ratio in the range from 90/10 to 50/50), butyl rubber, polyisobutylene rubber, styrene/butadiene rubber (SBR) and its hydrogenation product (H-SBR), styrene/butadiene block-copolymer rubber (SBS) and its hydrogenation product (SEBS), styrene/isoprene block-copolymer rubber (SIS) and its hydrogenation product (SEPS, HV-SIS), nitrile rubber (NBR), natural rubber (NR) and silicone rubber.

【 0020 】

When these rubbers other than the ethylene/ $\alpha$ -olefin copolymer rubber (a-2) are employed in a combination with the ethylene/ $\alpha$ -olefin copolymer rubber (a-2), the rubber other than the ethylene/ $\alpha$ -olefin copolymer



rubber (a-2) may favorably be incorporated in a proportion of 5 - 100 parts by weight, preferably 5 - 40 parts by weight, per 100 parts by weight of the total sum of the ethylene/ $\alpha$ -olefin copolymer rubber (a-2) and the polyolefin resin (a-1).

【 0021 】

The olefinic thermoplastic elastomer (A) may be compounded with the softening agent (a-3). As the softening agent (a-3), those which are used usually in rubbers may be employed, while preference is given in particular to those based on mineral oil and synthetic ones.

For the softening agent based on mineral oil, there may be recited, for example, lubricating oils based on petroleum, such as paraffinic, naphthenic and aromatic ones, and liquid paraffin. For the synthetic softening agent, there may be recited, for example, polyethylene wax, polypropylene wax, petroleum asphalt and vaseline.

【 0022 】

For other softening agents other than the above, there may be exemplified tars, such as coal tar and coal tar pitch; fatty oils, such as castor oil, linseed oil, rape oil, soybean oil and coconut oil; waxes, such as tall oil, beeswax, carnauba wax and lanolin; fatty acids, such as ricinoleic acid, palmitic acid, stearic acid, 12-hydroxystearic acid, montanic acid, oleic acid and erucic acid, and metal salts thereof; synthetic highpolymeric substances, such as petroleum resin, cumarone-indene resin and atactic polypropylene; plasticizers based on ester, such as dioctyl phthalate,

dioctyl adipate and dioctyl sebacate; and others including microcrystalline wax, liquid polybutadiene and its modified and hydrogenated products and liquid Thiokol.

【 0023 】

The softening agent (a-3) may favorably be employed in an amount of 5 - 200 parts by weight, preferably 15 - 150 parts by weight, more preferably 20 - 80 parts by weight, per 100 parts by weight of the ethylene/ $\alpha$ -olefin copolymer rubber (a-2). When the softening agent (a-3) is used in the proportion given above, it is made possible to improve the flowability of the foamable olefinic composition ( $X_1$ ) sufficiently without debasing the material properties, such as the heat resistance and the tensile strength, of the foamed body ( $X_2$ ).

The softening agent (a-3) may be added upon the production of the olefinic thermoplastic elastomer (A) or may preliminarily be admixed as an extender oil to, for example, the ethylene/ $\alpha$ -olefin copolymer rubber (a-2).

【 0024 】

The olefinic thermoplastic elastomer (A) is easy in recycled utilization, since it is not a thermosetting type elastomer such as the conventionally used vulcanized rubber, but is a thermoplastic elastomer.

To the olefinic thermoplastic elastomer (A) to be used according to the present invention, there may be admixed on requirement various additives known per se, such as heat resisting stabilizer, antioxidant, weathering stabilizer, antistatic agent, filler, coloring agent and

lubricant, within the range not obstructing the purpose of the present invention.

【 0025 】

○ Production of the olefinic thermoplastic elastomer (A)

The olefinic thermoplastic elastomer (A) to be used according to the present invention can be obtained by subjecting a mixture of the polyolefin resin (a-1) with the ethylene/ $\alpha$ -olefin copolymer rubber (a-2) and the optionally incorporated softening agent (a-3) etc. to a dynamic heat treatment.

【 0026 】

For the olefinic thermoplastic elastomer (A), there may favorably be employed those which are obtained by subjecting a mixture composed of the polyolefin resin (a-1) and the ethylene/ $\alpha$ -olefin copolymer rubber (a-2) with occasionally incorporated ingredient(s), such as the softening agent and so on, to a dynamic heat treatment in the presence of a cross-linking agent.

As the cross-linking agent which can be used upon the dynamic heat treatment, those which are usually employed in thermosetting rubbers may be used, such as organic peroxides, sulfur, phenolic resins, amino resins, quinone and its derivatives, compounds based on amine, azo compounds, epoxy compounds and isocyanates. Among them, especially, organic peroxides are preferred.

【 0027 】

As the organic peroxide, there may concretely be exemplified dicumyl peroxide, di-tert-butyl peroxide, 2,5-dimethyl-2,5-di-(tert-butylperoxy)hexane,

2,5-di-methyl-2,5-di-(tert-butylperoxy)hexyne-3,  
1,3-bis(tert-butylperoxyisopropyl)benzene,  
1,1-bis(tert-butylperoxy)-3,3,5-trimethylcyclohexane,  
n-butyl-4,4-bis(tert-butyl-peroxy) valerate, benzoyl  
peroxide, p-chlorobenzoyl per-oxide, 2,4-dichlorobenzoyl  
peroxide, tert-butyl peroxy-benzoate, tert-butyl  
perbenzoate, tert-butylperoxyiso-propyl carbonate,  
diacetyl peroxide, lauloyl peroxide and tert-butylcumyl  
peroxide.

【 0028 】

Among them, preference is given, in view of odour  
and scorching stability, to  
2,5-dimethyl-2,5-di-(tert-butylperoxy)hexane,  
2,5-dimethyl-2,5-di-(tert-butyl-peroxy)hexyne-3,  
1,3-bis(tert-butylperoxyisopropyl)-benzene,  
1,1-bis(tert-butylperoxy)-3,3,5-trimethylcyclo-hexane  
and n-butyl-4,4-bis(tert-butylperoxy) valerate, wherein,  
in particular, 1,3-bis(tert-butylperoxyiso-propyl)benzene  
is at most preferred.

According to the present invention, the organic  
peroxide is used in an amount of 0.05 - 3 parts by weight,  
preferably 0.1 - 2 prats by weight, per 100 parts by  
weight of the mixture of the polyolefin resin (a-1) and  
the ethylene/ $\alpha$ -olefin copolymer rubber (a-2) with  
occasionally incorporated ingredient(s), such as the  
softening agent etc.

【 0029 】

For the cross linking treatment using the organic  
peroxide, it is possible to incorporate an assistant for  
the peroxy-cross linking, such as sulfur,

p-quinonedioxime, p,p'-dibenzoylquinonedioxime,  
N-methyl-N-4-dinitrosoaniline, nitrosobenzene,  
diphenyl-guanidine and  
trimethylolpropane-N,N'-m-phenylenedi-maleimide, or a  
polyfunctional methacrylate monomer, such as  
divinylbenzene, triallyl cyanurate, ethylene glycol  
dimethacrylate, diethylene glycol dimethacrylate,  
polyethylene glycol dimethacrylate, trimethylolpropane  
trimethacrylate or allyl methacrylate, or, further, a  
polyfunctional vinyl monomer, such as vinyl butyrate or  
vinylstearate.

【 0030 】

By using the compound as above, a uniform and mild cross-linking reaction can be expected. In particular, divinylbenzene is at most preferable for the present invention. Divinylbenzene is easy in handling, has a better compatibility with the polyolefin resin (a-1) and the ethylene/ $\alpha$ -olefin copolymer rubber (a-2) constituting main components of the material to be cross-linked and reveals a function of solubilizing the organic peroxide to act as a dispersant, so that an olefinic thermoplastic elastomer (A) exhibiting uniform cross-linking effect by the heat treatment and having a better balance between the flowability and the material properties can be obtained.

【 0031 】

The above-mentioned cross-linking assistant or the polyfunctional vinyl monomer may favorably be used in an amount in the range from 0.1 to 3 % by weight, preferably from 0.3 to 2 % by weight, based on the total

weight of the mass to be cross-linked. When the amount of the cross-linking assistant or the polyfunctional vinyl monomer is in the above-mentioned range, not only the cross-linking assistant but also the polyfunctional vinyl monomer will never remain in the elastomer as unreacted monomer, so that the resulting thermoplastic elastomer does not suffer from alteration of the material properties due to the heating hysteresis and is superior in the flowability.

【 0032 】

The word "dynamic heat treatment" means that the components given above are kneaded in a molten state (fused state).

As the kneading apparatus, known ones, such as for example, open-type mixing roll and non-open type ones, such as Bumbury's mixer, extruder, kneader and continuous mixer, may be employed. Among them, non-open type kneading apparatuses are preferred, wherein the kneading procedure may favorably be effected under an inert gas atmosphere, such as nitrogen gas or carbon dioxide gas.

【 0033 】

The temperature upon the dynamic heat treatment may usually be at 150 - 280 °C, preferably 170 - 240 °C, and the kneading duration may favorably be 1 - 20 minutes, preferably 1 - 5 minutes. The shearing force imposed may favorably be 10 - 1,000 sec<sup>-1</sup>; preferably 100 - 1,000 sec<sup>-1</sup>, in terms of shearing velocity.

【 0034 】

The olefinic thermoplastic elastomer (A) to be used

desirably according to the present invention may favorably have a gel content, as calculated in the manner given below, of 10 % by weight or higher, preferably 20 % by weight or higher, especially preferably 45 % by weight or higher. When the gel content is 10 % by weight or higher, the resulting foamed body (X<sub>2</sub>) exhibits superior rubbery properties, such as heat resistance, tensile strength, flexibility, weatherability and repulsive resilience, and is suitable for recycled utilization.

【 0035 】

《 Method for determining the gel content 》

About 100 mg of a sample of the thermoplastic elastomer are weighed off and cut into grains of a size of 0.5 mm × 0.5 mm × 0.5 mm and the resulting grains are soaked in 30 ml of cyclohexane in a sealed vessel at 23 °C for 48 hours. The so-soaked granular sample is taken out on a filter paper and is dried at room temperature for over 72 hours until a constant weight is reached.

The value calculated by subtracting the weight of cyclohexane-insoluble ingredients other than the polymer components (for example, fibrous filler, filler and pigments) from the weight of the above dried residual matter is regarded as the "corrected final weight of (Y)".

On the other hand, the value calculated by subtracting the weight of cyclohexane-soluble ingredients other than the polymer components (for example, softening agent) and the weight of cyclohexane-insoluble ingredients other than the polymer components (for example, fibrous filler, filler and

pigments) from the weight of the above dried residual matter is regarded as the "corrected initial weight of (X)".

【 0036 】

The gel content (content of cyclohexane-insoluble polymer) is calculated by the equation:

Gel cont. (wt. %) =

$$[\text{corrected final wt. (Y)}] \div [\text{corrected init. wt. (X)}] \times 100$$

【 0037 】

○ The olefinic thermoplastic resin (B)

The olefinic thermoplastic resin (B) to be used according to the present invention is a polymeric or copolymeric product having an olefin content in the range from 50 to 100 mole %, preferably from 60 to 100 mole %, and an MFR (ASTM D-1238-65T, 230 °C, 2.16 kg load) in the range from 0.01 to 2 g/10 min., preferably from 0.02 to 2 g/10 min. As the olefinic thermoplastic resin (B), there may be recited, for example, the polyolefin resin (a-1) which satisfy the above-mentioned material property condition.

For the olefinic thermoplastic resin (B), homopolymers of propylene and propylene/ $\alpha$ -olefin copolymers having propylene contents of at least 50 mole %, preferably in the range from 60 to 95 mole %, are especially favorable.

【 0038 】

Due to that the MFR value of the olefinic thermoplastic resin (B) is within the range from 0.01 to 2 g/10 min., the melt tension of the resulting foamable olefinic composition (X<sub>1</sub>) can be held at a high value,



whereby a foamed body ( $X_2$ ) of higher foaming expansion ratio can be obtained.

The olefinic thermoplastic resin (B) may be incorporated either individually or in a combination of two or more kinds.

【 0039 】

The olefinic thermoplastic resin (B) may be used in an amount of 1 - 20 parts by weight, preferably 1 - 10 parts by weight, per 100 parts by weight of the olefinic thermoplastic elastomer (A). When the olefinic thermoplastic resin (B) is used in the above-mentioned amount, the resulting foamed body ( $X_2$ ) is superior in the flexibility.

【 0040 】

The olefinic thermoplastic elastomer (B) of the present invention is characterized in that it is used concurrently with the olefinic thermoplastic elastomer (A) produced through a dynamic heat treatment, while the olefinic thermoplastic resin (B) itself is not subjected to any dynamic heat treatment. When, on the production of the olefinic thermoplastic elastomer (A), the polyolefin resin (a-1) and the ethylene/ $\alpha$ -olefin copolymer rubber (a-2), mixed with an organic peroxide etc., are kneaded with heating, while admixing thereto the olefinic thermoplastic resin (B), any contemplated foamed body ( $X_2$ ) may, according to certain kind of the olefinic thermoplastic resin (B), not be obtained, because of that the olefinic thermoplastic resin (B) may be subjected to thermal decomposition into lower molecular weight products or due to that a gellation may occur by cross

linking by heat.

【 0041 】

○ The foaming agent (C)

As the foaming agent (C) to be blended to the raw material of the substrate layer, there may be recited, for example, organic and inorganic thermal decomposition type foaming agents; water; solvents, such as those based on hydrocarbon and halogenated hydrocarbon; and gases, such as nitrogen gas, carbon dioxide gas, propane and butane. As the foaming agent (C), organic and inorganic thermal decomposition type foaming agents, water, carbon dioxide and so on are preferred.

【 0042 】

As the inorganic foaming agent of thermal decomposition type, there may be recited concretely, for example, sodium hydrogencarbonate, sodium carbonate, ammonium hydrogencarbonate, ammonium carbonate and ammonium nitrite.

As the organic foaming agent of thermal decomposition type, there may be recited concretely, for example, nitroso compounds, such as N,N'-dimethyl-N,N'-dinitrosoterephtharamide and N,N'-dinitrosopenta-methylenetetramine (DPT); azo compounds, such as azodicarbonamide (ADCA), azobisisobutyronitrile (AZBN), azobiscyclohexylnitrile, azodiaminobenzene and barium azodicarboxylate; sulfonylhydrazides, such as benzenesulfonylhydrazide (BSH), toluenesulfonylhydrazide (TSH), p,p'-oxybis(benzenesulfonylhydrazide) (OBSh) and diphenylsulfon-3,3'-disulfonylhydrazide; and azides,

such as calcium azide, 4,4'-diphenyldisulfonyl azide and p-toluenesulfonyl azide.

【 0043 】

The foaming agent (C) may be used individually or in a combination of two or more kinds.

The foaming agent (C) may favorably be used usually in an amount of 0.5 - 20 parts by weight, preferably 1 - 10 parts by weight, per 100 parts by weight of the olefinic thermoplastic elastomer (A).

【 0044 】

The foamable olefinic composition ( $X_1$ ) to be used according to the present invention may, on requirement, contain by admixing thereto a foaming assistant. As the foaming assistant, there may be incorporated metal-containing compounds having a metal, such as zinc, calcium, lead, iron or barium; organic acids, such as citric acid, salicylic acid, phthalic acid, stearic acid and oxalic acid; and urea and its derivatives. The foaming assistant may favorably be used usually in an amount of 0.1 - 20 parts by weight, preferably 1 - 10 parts by weight, per 100 parts by weight of the olefinic thermoplastic elastomer (A). The foaming assistant provides functions for, for example, lowering the decomposition temperature of the foaming agent, accelerating the decomposition and forming homogeneous foams.

【 0045 】

The foamable olefinic composition ( $X_1$ ) may contain, if necessary, by admixing thereto, for example, an inorganic porous powdery substance, such as zeolite, a

resin exhibiting higher adsorptivity for inorganic gases, such as polycarbonate resin, and nucleating agent for foaming.

【 0046 】

The foamable olefinic composition ( $X_1$ ) may further contain, if necessary, by admixing thereto, various known additives, for example, filler, heat resisting stabilizer, antioxidant, weathering stabilizer, antistatic agent, wetting agent, lubricant, such as metal soap or wax, pigment, dyestuff, fire retarding agent and blocking inhibitor, within the range not obstructing the purpose of the present invention.

【 0047 】

As the filler to be blended with the foamable olefinic composition ( $X_1$ ), those which are incorporated usually in rubbers may favorably be used. Concretely, there may be recited, for example, calcium carbonate, calcium silicate, clay, kaolin, talc, silica, diatomaceous earth, powdery mica, asbestos, barium sulfate, aluminum sulfate, calcium sulfate, magnesium carbonate, molybdenum disulfide, glass fiber, glass beads, Shirasu balloon, graphite and alumina.

The filler may favorably be incorporated usually in an amount of 40 parts by weight or less, preferably 1 - 30 parts by weight, per 100 parts by weight of the olefinic thermoplastic elastomer (A).

【 0048 】

○ Preparation of the olefinic foamable composition ( $X_1$ )

The olefinic foamable composition ( $X_1$ ) may be

prepared by compounding the olefinic thermoplastic elastomer (A), the olefinic thermoplastic resin (B) and the foaming agent (C) together with the optionally incorporated other ingredients, such as the foaming assistant and wetting agent. For the compounding, a method may be used, in which the olefinic thermoplastic elastomer (A) is mixed with the olefinic thermoplastic resin (B) and the foaming agent (C) and, if the optional ingredients, such as the foaming assistant and wetting agent, are to be incorporated, these optional ingredients are compounded upon blending the olefinic thermoplastic resin (B) and the foaming agent (C). The olefinic thermoplastic resin (B) and the foaming agent (C) may be compounded either simultaneously or each individually. In the case of compounding individually, the olefinic thermoplastic elastomer (A) is first mixed with the olefinic thermoplastic resin (B) and, then, the foaming agent (C) is admixed thereto, though the mixing sequence may be reversed.

【 0049 】

If the olefinic thermoplastic resin (B) and/or the foaming agent (C) is compounded on the production of the olefinic thermoplastic elastomer (A), no contemplated foamed body ( $X_2$ ) can be obtained. When the olefinic thermoplastic resin (B) and/or the foaming agent (C) is compounded upon the production of the olefinic thermoplastic elastomer (A), the olefinic thermoplastic resin (B) may, according to certain kind of the olefinic thermoplastic resin (B), be pyrolyzed into lower molecular products or a gellation due to cross

linking may occur by heat, whereby the melt viscosity may become greatly deviated from the value necessary for obtaining the contemplated foamed body ( $X_2$ ) or a phenomenon of blowing off may occur on decomposition of the foaming agent (C).

【 0050 】

For concrete practice of compounding the olefinic thermoplastic elastomer (A), the olefinic thermoplastic resin (B) and the foaming agent (C), there may be used, for example, a method, in which a pelletized product of the olefinic thermoplastic elastomer (A), the olefinic thermoplastic resin (B) and the foaming agent (C) are once kneaded on, for example, a tumbler type Bravender, V-shaped Bravender, a ribbon blender or a Henschel mixer, followed by, if necessary, further kneading on an open type mixing roll or on a non-open type kneading apparatus, such as Bumbury's mixer, extruder, kneader or continuous mixer.

The weathering stabilizer, heat-resisting stabilizer, antioxidant, pigment, dyestuff and so on may be blended at any process step given above.

【 0051 】

The substrate layer to be used according to the present invention is a foamed body ( $X_2$ ) of the above-mentioned foamable olefinic composition ( $X_1$ ) and can be obtained, for example, by a method of heating the foamable olefinic composition ( $X_1$ ):

【 0052 】

For the raw material of the skin layer, at least one kind selected from the raw materials based on olefin

given in the following 1) to 4) may be employed according to the present invention:

1) The ultrahigh molecular weight polyolefin resin (Y) mentioned previously which is an ultrahigh molecular weight polyolefin resin having an intrinsic viscosity ( $\eta$ ) of 3.5 - 8.3 dl/g, as determined in decalin of 135 °C.

2) An olefinic thermoplastic elastomer composition ( $Z_1$ ) containing, per 100 parts by weight of the olefinic thermoplastic elastomer (D), at least one selected from the group consisting of 0.5 - 25 parts by weight of an organopolysiloxane (E), 0.5 - 10 parts by weight of a fluorine-containing polymer (F) and 0.5 - 10 parts by weight of an antistatic agent (G), each in the given proportion.

3) An olefinic thermoplastic elastomer composition ( $Z_2$ ) containing a polyolefin resin (H) in an amount of 5 - 200 parts by weight, per 100 parts by weight of the olefinic thermoplastic elastomer (D).

4) An olefinic thermoplastic elastomer composition ( $Z_3$ ) containing, per 100 parts by weight of the olefinic thermoplastic elastomer (D), at least one selected from the group consisting of 0.5 - 25 parts by weight of an organopolysiloxane (E), 0.5 - 10 parts by weight of a fluorine-containing polymer (F) and 0.5 - 10 parts by weight of an antistatic agent (G), each in the given proportion, and further a polyolefin resin (H) in an amount of 5 - 200 parts by weight.

【 0053 】

○ The ultrahigh molecular weight polyolefin resin (Y)  
The ultrahigh molecular weight polyolefin resin (Y)

to be used as the raw material of the skin layer according to the present invention is an ultrahigh molecular weight polyolefin resin having an intrinsic viscosity ( $\eta$ ) in the range from 3.5 to 8.3 dl/g, preferably from 3.8 to 8.0 dl/g, as determined in decalin of 135 °C. The ultrahigh molecular weight polyolefin resin (Y) may either consist of a single kind of resin or a composition comprising two or more resins. For the case of the resin composition, one which has an intrinsic viscosity ( $\eta$ ) as the entire composition within the above-mentioned range may be employed.

【 0054 】

In the case where the ultrahigh molecular weight polyolefin resin (Y) is a resin composition, an ultrahigh molecular weight polyolefin resin composition comprising an ultrahigh molecular weight polyolefin resin (y-1) having an intrinsic viscosity ( $\eta$ ) of 10 - 40 dl/g, as determined in decalin of 135 °C, and a polyolefin resin (y-2) having an intrinsic viscosity ( $\eta$ ) of 0.1 - 5 dl/g, as determined in decalin of 135 °C, is favorable and, further, such an ultrahigh molecular weight polyolefin resin composition may be more favorable, which contains 15 - 40 parts by weight of the ultrahigh molecular weight polyolefin resin (y-1) and 60 - 85 parts by weight of the polyolefin resin (y-2), and particularly favorable one contains 18 - 35 parts by weight of the ultrahigh molecular weight polyolefin resin (y-1) and 65 - 82 parts by weight of the polyolefin resin (y-2), with the total of the two summing up to 100 parts by weight.



## 【 0055 】

As the ultrahigh molecular weight polyolefin resin (y-1) and the polyolefin resin (y-2), there may be recited, for example, homopolymers and copolymers of  $\alpha$ -olefins, such as ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 1-octene, 1-decene, 1-dodecene, 4-methyl-1-pentene and 3-methyl-1-pentene. For the ultrahigh molecular weight polyolefin resin (y-1) and for the polyolefin resin (y-2), copolymers composed mainly of ethylene, namely, homopolymers of ethylene and copolymers of ethylene with other  $\alpha$ -olefin, are preferred.

## 【 0056 】

The ultrahigh molecular weight polyolefin resin (Y) may contain a liquid or solid softening agent (lubricating oil).

As the liquid softening agent to be admixed to the ultrahigh molecular weight polyolefin resin (Y), those based on mineral oil and synthetic ones are used. Concretely, there may be enumerated, for example, paraffinic and naphthenic lubricant oils, liquid paraffin, spindle oil, refrigerator oil, dynamo oil, turbine oil, machine oil and cylinder oil. As the synthetic lubricant oils, there may be recited concretely synthetic hydrocarbon oils, polyglycol oils, polyphenyl ether oils, ester oils, phosphate oils, polychlorotrifluoroethylene oils, fluoroester oils, chlorinated biphenyl oils and silicone oils.

## 【 0057 】

As the solid softening agent, concretely, grafite and

molybdenum disulfide are used principally, though otherwise boron nitride, wolfrum disulfide, lead oxide, glass powder, metal soaps and so on may also be used.

The softening agent may be incorporated either individually or in a combination of two or more kinds in a form of, for example, powder, sol, gel or suspensoid.

【 0058 】

The content of the softening agent may favorably be in the range from 1 to 20 parts by weight, preferably from 3 to 15 parts by weight, per 100 parts by weight of the ultrahigh molecular weight polyolefin resin (Y).

There may be compounded with the ultrahigh molecular weight polyolefin resin (Y), if necessary, additives, such as heat-resisting stabilizer, antistatic agent, weathering stabilizer, antioxidant, filler, coloring agent and lubricant, within the range not obstructing the purpose of the present invention.

【 0059 】

○ The olefinic thermoplastic elastomer compositions (Z<sub>1</sub>) to (Z<sub>3</sub>)

○ The olefinic thermoplastic elastomer (D)

According to the present invention, there may be incorporated, for the olefinic thermoplastic elastomer (D) to be used as the raw material of the skin layer, for example, an olefinic thermoplastic elastomer composed of a crystalline polyolefin resin (d-1) and a rubber (d-2).

【 0060 】

As the crystalline polyolefin resin (d-1), there may be enumerated, for example, homopolymers and copolymers of  $\alpha$ -olefins having 2 - 20 carbon atoms.

Concrete examples of the crystalline polyolefin (d-1) include (co)polymers given below:

1) Homopolymers of ethylene (obtained either by low pressure and high pressure processes)

2) Copolymers of ethylene with 10 mole % or less, of other  $\alpha$ -olefin or vinyl monomer, such as vinyl acetate or ethyl acrylate

3) Homopolymers of propylene

4) Random copolymers of propylene with 10 mole % or less, of other  $\alpha$ -olefins

5) Block-copolymers of propylene with 30 mole % or less of other  $\alpha$ -olefins

6) Homopolymers of 1-butene

7) Random copolymers of 1-butene with 10 mole % or less, of other  $\alpha$ -olefins

8) Homopolymers of 4-methyl-1-pentene

9) Random copolymers of 4-methyl-1-pentene with 20 mole % or less, of other  $\alpha$ -olefins

As the above  $\alpha$ -olefins, there may concretely be exemplified ethylene, propylene, 1-butene, 4-methyl-1-pentene, 1-hexene and 1-octene.

【 0061 】

As the crystalline polyolefin resin (d-1), there may favorably be enumerated homopolymers of propylene and copolymers of propylene used as principal component with another olefin, for example, propylene/ethylene copolymer, propylene/1-butene copolymer, propylene/1-hexene copolymer and propylene/4-methyl-1-pentene copolymer.

The crystalline polyolefin resin (d-1) may favorably

have an MFR (ASTM D-1238, 230 °C, 2.16 kg load) in the range from 0.01 to 100 g/10 min., preferably from 0.1 to 50 g/10 min.

【 0062 】

There is no special limitation as to the rubber (d-2) to be used according to the present invention, though preference is given to olefinic copolymer rubbers.

For the olefinic copolymer rubber to be used as the rubber (d-2), there may be exemplified amorphous random elastomeric copolymers each having, as a main component, an  $\alpha$ -olefin having 2 - 20 carbon atoms, such as non-crystalline  $\alpha$ -olefin copolymers each constituted of at least two  $\alpha$ -olefins and  $\alpha$ -olefin/non-conjugated polyene copolymers each constituted of at least two  $\alpha$ -olefins and non-conjugated diene(s).

【 0063 】

As concrete examples of the olefinic copolymer rubbers to be used as the rubber (d-2), the rubbers, such as those given above may be recited:

1) Copolymer rubbers of ethylene/ $\alpha$ -olefin having ethylene/ $\alpha$ -olefin mole ratios of about 90/10 to 50/50

2) Copolymer rubbers of ethylene/ $\alpha$ -olefin/non-conjugated diene having ethylene/ $\alpha$ -olefin mole ratios of about 90/10 to 50/50

3) Copolymer rubbers of propylene/ $\alpha$ -olefin having the mole ratio propylene/ $\alpha$ -olefin of about 90/10 to 50/50

4) Copolymer rubbers of butene/ $\alpha$ -olefin having butene / $\alpha$ -olefin mole ratios of about 90/10 to 50/50

【 0064 】

As the  $\alpha$ -olefin, there may concretely be exemplified those which are the same as the concretely exemplified  $\alpha$ -olefins constituting the crystalline polyolefin (d-1) given above.

As the non-conjugated dienes, there may concretely be exemplified dicyclopentadiene, 1,4-hexadiene, cyclooctadiene; methylenenorbornene, ethylenenorbornene and so on.

The rubber (d-2) may be used either individually or in a combination of two or more kinds.

【 0065 】

As the rubber (d-2), concretely, there may favorably be used ethylene/propylene copolymer rubbers, ethylene/propylene/non-conjugated polyene copolymer rubbers, ethylene/1-butene copolymer rubbers and ethylene/1-butene/non-conjugated polyene rubbers, with special preference to ethylene/propylene/non-conjugated polyene copolymer rubbers, in particular, ethylene/propylene/ethylidenenorbornene copolymer rubber and ethylene/propylene/cyclopentadiene copolymer rubber.

These copolymer rubbers may favorably have Mooney viscosities  $ML_{1+4}(100\text{ }^{\circ}\text{C})$  in the range from 10 to 250, preferably from 40 to 150. For the case where the above non-conjugated polyene is co-polymerized, they may favorably have iodine values of 25 or lower.

【 0066 】

For the rubber (d-2) to be used according to the present invention, there may also be recited other rubbers, for example, rubbers based on diene, such as

styrene/butadiene rubber (SBR), nitrile rubbers (NBR), natural rubber (NR) and butyl rubber (IIR), and SEBS as well as polyisobutylenes.

【 0067】

In the olefinic thermoplastic elastomer (D) to be used according to the present invention, the weight proportion of the crystalline polyolefin resin (d-1) to the rubber (d-2), namely, [crystalline polyolefin resin]/[rubber], may favorably be in the range of usually from 90/10 to 5/95, preferably from 70/30 to 10/90.

In the case of using, as the rubber (d-2), the olefinic copolymer rubber in combination with other rubber, it is favorable to incorporate the said other rubber in an amount of 40 parts by weight or less, preferably in the range from 5 to 20 parts by weight, per 100 parts by weight of the total sum of the crystalline polyolefin resin (d-1) and the rubber (d-2).

【 0068】

If necessary, the olefinic thermoplastic elastomer (D) may be compounded with additives, such as softening agent, heat-resisting stabilizer, weathering stabilizer, antioxidant, filler, coloring agent and lubricant, within the range not obstructing the purpose of the present invention.

As the softening agent, those used usually for rubbers may be employed, wherein preference is given to those based on mineral oil and to synthetic ones.

【 0069】

As the softening agent based on mineral oil to be compounded with the olefinic thermoplastic elastomer

(D), for example, lubricating oils based on petroleum, such as paraffinic, naphthenic and aromatic ones, and liquid paraffin are recited. As the synthetic softening agent, there may be recited, for example, polyethylene wax, polypropylene wax, petroleum asphalt and vaseline.

For other softening agents, there may be recited, for example, coal tars, such as coal tar and coal tar pitch; fatty oils, such as castor oil, line seed oil, rape oil, soybean oil and coconut oil; waxes, such as tall oil, beeswax, carnauba wax and lanoline; fatty acids, such as ricinoleic acid, palmitic acid, stearic acid, 12-hydroxystearic acid, montanic acid, oleic acid and erucic acid, as well as their metal salts; synthetic polymer products, such as petroleum resin, cumarone-indene resin and atactic polypropylene; plasticizers based on ester, such as dioctyl phthalate, dioctyl adipate and dioctyl sebacate; others including microcrystalline wax, liquid polybutadiene and modified and hydrogenated products thereof, and liquid Thiokol.

【 0070 】

These softening agents may favorably be used in a proportion of 5 - 200 parts by weight, preferably 15 - 150 parts by weight, more preferably 20 - 80 parts by weight, per 100 parts by weight of the olefinic thermoplastic elastomer (D).

The softening agent may be added to the olefinic thermoplastic elastomer (D) during the production thereof or may have been admixed beforehand to the rubber (d-2) in a form of an extender oil.

【 0071 】

The olefinic thermoplastic elastomer (D) to be used according to the present invention can be obtained by subjecting a mixture of the polyolefin resin (d-1) and the rubber (d-2), with occasionally incorporated softening agent etc., to the dynamic heat treatment.

The rubber (d-2) may be present in the olefinic thermoplastic elastomer (D) in non-cross-linked state or in every cross-linked state from a partially cross-linked state to the fully cross-linked state.

【 0072 】

For producing the olefinic thermoplastic elastomer (D) in such a cross-linked state, it is favorable to subject a mixture of the polyolefin resin (d-1) and the rubber (d-2) with the optionally added ingredients, such as the softening agent etc., to a dynamic heat treatment in the presence of a cross linking agent. The method of the dynamic heat treatment is the same as the method for the olefinic thermoplastic elastomer (A).

【 0073 】

The olefinic thermoplastic elastomer (D) to be used favorably according to the present invention may favorably have a gel content, as calculated according to the procedures given above, of 10 % by weight or higher, preferably 20 % by weight or higher, especially preferably 45 % by weight or higher.

【 0074 】

As the olefinic thermoplastic elastomer (D) to be used for the skin layer according to the present invention, the above-mentioned ethylenic thermoplastic elastomer (A) can also be employed.



The olefinic thermoplastic elastomer (D) constituting the skin layer of the foamed laminate based on olefin according to the present invention is constituted of the crystalline polyolefin resin (d-1) and the rubber (d-2) and, therefore, is superior in the flowability.

Such a polyolefinic thermoplastic elastomer (D) can be formed on conventionally employed molding apparatuses by, for example, compression molding, transfer molding, injection molding and extrusion molding.

【 0075 】

○ The organopolysiloxane (E)

As the organopolysiloxane (E) to be used for the raw material of the skin layer according to the present invention, known organopolysiloxanes having -Si-O-bonds in the main chain may be used without any restriction. By incorporating organopolysiloxane (E), a skin layer exhibiting superior sliding performance and superior abrasion resistance can be obtained.

【 0076 】

As the organopolysiloxane (E), there may be recited concretely, for example, dimethylpolysiloxane, methylphenylpolysiloxane, fluoropolysiloxane, tetramethyl-tetraphenylpolysiloxane and methylhydrogenpolysiloxane, as well as modified polysiloxanes, such as epoxy-modified, alkyl-modified, amine-modified, carboxyl-modified, alcohol-modified, fluorine-modified, alkyl-aralkylpolyether-modified and epoxypolyether-modified ones. Among them, preference is given to dimethylpolysiloxane. The

organopolysiloxane (E) can be used either individually or in a combination of two or more kinds.

【 0077 】

For the organopolysiloxane (E), those which have viscosity values (as determined according to JIS K 2283 at 25 °C) in the range from 10 to  $10^7$  cSt are preferred. Among them, those having viscosity values (JIS K 2283 at 25 °C) of  $10^6$  or higher may be formulated as a masterbatch with olefinic resin(s) for enhancing the dispersibility in the olefinic thermoplastic elastomer (D), as they have a very high viscosity. As the olefinic resin to be used here, the crystalline polyolefin resin (d-1) used for preparing the olefinic thermoplastic elastomer (D) is recited and, concretely, there may be recited, for example, homopolymers of ethylene, copolymers of ethylene with other  $\alpha$ -olefins, homopolymers of propylene and copolymers of propylene with other  $\alpha$ -olefins.

【 0078 】

The organopolysiloxane (E) may be incorporated either individually or in a combination of two or more kinds in accordance with the viscosity thereof. In particular, in the case of using two or more kinds in combination, it is preferable to use a combination of a lower viscosity organopolysiloxane (E) having a viscosity of 10 -  $10^6$  cSt with a higher viscosity organopolysiloxane (E) having a viscosity of  $10^6$  -  $10^7$  cSt.

【 0079 】

In the olefinic thermoplastic elastomer composition

(Z<sub>1</sub>), the organopolysiloxane (E) may be contained in a proportion of 0.5 - 20 parts by weight, preferably 1 - 18 parts by weight, per 100 parts by weight of the olefinic thermoplastic elastomer (D). If the content of the organopolysiloxane (E) is in the above range, the resulting foamed laminate is superior in the sliding performance and there occurs no inconvenience due to, for example, sticky hand touch of the surface by the organopolysiloxane (E).

【 0080 】

○ The fluorine-containing polymer (F)

As the fluorine-containing polymer (F) to be used according to the present invention, known polymers having fluorine atom may be employed without any restriction. By addition of the fluorine-containing polymer (F), the skin layer becomes superior in the sliding performance and in the abrasion resistance.

As the fluorine-containing polymer (F) to be used according to the present invention, there may be enumerated, for example, polytetrafluoroethylene, tetra-fluoroethylene/hexafluoropropylene copolymer, tetra-fluoroethylene/perfluorovinyl ether copolymer, tetra-fluoroethylene/ethylene copolymer, polymers of vinylidene fluoride and polymers of vinyl fluoride. The fluorine-containing polymer (F) may be incorporated either individually or in a combination of two or more kinds.

【 0081 】

The fluorine-containing polymer (F) may be formulated preliminarily as a masterbatch with olefinic

resin(s) and/or with known inorganic filler(s), in order to facilitate the dispersibility in the olefinic thermoplastic elastomer (D) or to further increase the effect of improving the sliding performance. As the olefinic resin to be used here, those which are the same as used in the masterbatch for the organosiloxane (E) may be enumerated. As the inorganic filler, there may be recited, for example, calcium carbonate, titanium oxide, talc and clay.

【 0082 】

In the olefinic thermoplastic elastomer composition ( $Z_1$ ), the fluorine-containing polymer (F) may be contained in a proportion of 0.5 - 10 parts by weight, preferably 1 - 8 parts by weight, per 100 parts by weight of the olefinic thermoplastic elastomer (D). When the content of the fluorine-containing polymer (F) is in the above range, the resulting foamed laminate is superior in the sliding performance.

【 0083 】

○ The antistatic agent (G)

For the antistatic agent (G) to be used according to the present invention, known antistatic agents used in general for resins may be employed without any restriction, examples of which include anionic surfactants, cationic surfactants, non-ionic surfactants and ampholytic surfactants. By incorporating the antistatic agent (G), the resulting skin layer becomes superior in the sliding performance and in the abrasion resistance.

【 0084 】

Concrete examples of the antistatic agent (G) include lauryldiethanolamine, N,N-bis(2-hydroxyethyl)-stearylamine, stearyl monoglyceride, distearyl glyceride, tristearyl glyceride, polyoxyethylene-laurylamine capryl ester and stearyldiethanolamine monoesterate. The antistatic agent (G) may be used either individually or in a combination of two or more kinds.

【 0085 】

The antistatic agent (G) may be formulated preliminarily as a masterbatch with olefinic resin(s) and/or with known inorganic filler(s), in order to facilitate the dispersibility in the olefinic thermoplastic elastomer (D) or to further increase the effect of improving the sliding abrasion resistance. As the olefinic resin and the inorganic filler to be used here, those which are the same as those mentioned above may be enumerated.

【 0086 】

In the olefinic thermoplastic elastomer composition ( $Z_1$ ), the antistatic agent (G) may be contained in a proportion of 0.5 - 10 parts by weight, preferably 1 - 8 parts by weight, per 100 parts by weight of the olefinic thermoplastic elastomer (D). When the content of the antistatic agent (G) is in the above range, the resulting foamed laminate is superior in the sliding performance and there occurs no inconvenience due to, for example, whitening by deposition of the antistatic agent (G) on the surface (bleeding out).

【 0087 】

The organopolysiloxane (E), the fluorine-containing polymer (F) and the antistatic agent (G) may each be used either individually or in a combination of two or more kinds, wherein the combination is arbitrary.

【 0088 】

○ The polyolefin resin (H)

As the polyolefin resin (H) to be used according to the present invention, the crystalline polyolefin resin (d-1) used for the olefinic thermoplastic elastomer (D) may favorably be employed. Also, the ultrahigh molecular weight polyolefin resin (Y) described previously may be employed for the polyolefin resin (H) to be used according to the present invention.

【 0089 】

In the olefinic thermoplastic elastomer composition (Z<sub>2</sub>), the polyolefin resin (H) may be contained in a proportion of 5 - 200 parts by weight, preferably 10 - 180 parts by weight, per 100 parts by weight of the olefinic thermoplastic elastomer (D). When the olefinic thermoplastic elastomer (D) and the polyolefin resin (H) are used in such a proportion, the skin layer obtained exhibits better moldability and better molding appearance and is superior in the sliding performance and in the abrasion resistance.

【 0090 】

The polyolefin resin (H) can be incorporated concurrently with at least one selected from the group consisting of the organopolysiloxane (E), fluorine-containing polymer (F) and the antistatic agent (G). The amount of each component (E) to (H) to be

contained in the olefinic thermoplastic elastomer composition ( $Z_3$ ) is as given above.

【 0091 】

There may be compounded with the olefinic thermoplastic elastomer compositions ( $Z_1$ ) to ( $Z_3$ ) to be used for the raw material of the skin layer, on requirement, additives, such as softening agent based on mineral oil, heat resisting stabilizer, weathering stabilizer, antioxidant, filler, coloring agent and lubricant, within the range not obstructing the purpose of the present invention.

【 0092 】

The olefinic thermoplastic elastomer compositions ( $Z_1$ ) - ( $Z_3$ ) can be produced by known techniques, for example, by kneading the olefinic thermoplastic elastomer (D) with at least one selected from the group consisting of the organopolysiloxane (E), the fluorine-containing polymer (F) and the antistatic agent (G), as well as with the polyolefin resin (H) and other optionally admixed additives.

【 0093 】

The foamed laminate based on olefin according to the present invention is a laminate produced by laminating a skin layer made of the ultrahigh molecular weight polyolefin resin (Y) or the olefinic thermoplastic elastomer compositions ( $Z_1$ ) to ( $Z_3$ ) on a substrate layer made of the foamed body ( $X_2$ ) of the foamable olefinic composition ( $X_1$ ) given above. The skin layer may be laminated on the substrate layer covering the entire area or partial area of the substrate layer or it is permissible

that other layer(s) is(are) laminated. In the case where skin layer is laminated covering a partial area of the substrate, the residual area not covered by the skin layer may be held exposed. The substrate layer and the skin layer may be laminated using an adhesive, though preferably they are fused together. While there is no special limitation as to the thickness of the foamed laminate, it is favorable that the substrate layer has a thickness of 0.1 - 50 mm, preferably 0.5 - 45 mm, and the skin layer has a thickness of 5  $\mu$ m - 10 mm, preferably 10  $\mu$ m - 8 mm. The foaming expansion ratio of the foamed body ( $X_2$ ) may favorably be in the range from 1.1 to 20 times, preferably from 2 to 10 times the original volume, though there is no special limitation therefor. According to the present invention, even foamed bodies ( $X_2$ ) having higher expansion ratios of 2 times or higher may easily be molded, since the olefinic thermoplastic resin (B) can foam up sufficiently.

【 0094 】

The foamed laminate based on olefin according to the present invention may exhibit a soft hand touch, since the substrate layer can be made at a high expansion ratio as indicated above and is superior in the appearance, abrasion resistance, durability and sliding performance. The foamed laminate according to the present invention can be produced in an easy manner and reveals a high economical efficiency due to permission of recycled utilization.

【 0095 】

The foamed laminate based on olefin according to the



present invention is obtained by providing the substrate layer of the foamed body ( $X_2$ ) of the foamable olefinic composition ( $X_1$ ) and making up the skin layer from the ultrahigh molecular weight polyolefin resin (Y) or the olefinic thermoplastic elastomer compositions ( $Z_1$ ) to ( $Z_3$ ) and laminating these layers. The practical manner of lamination may vary according to the shape, size, material properties required and so on, while there may favorably be exemplified a method in which the substrate layer and the skin layer are co-extruded simultaneously using a multilayer extrusion molding machine, followed by heat fusing them together. The foamable olefinic composition ( $X_1$ ) foams up upon the heat fusing under co-extrusion to form the foamed body ( $X_2$ ) which build up the substrate layer. Such a heat fusing technique requires no adhesive and permits to obtain a foamed laminate easily by a single process step in an easy manner, wherein the thereby obtained interlayer adhesion between the substrate layer and the skin layer is firm.

【 0096 】

The foamed laminate based on olefin according to the present invention can be used favorably, for example, for automobile parts, such as automobile weather strips, and for architectural materials, such as gaskets. For the automobile weather strips, there may be exemplified door weather strip, hood weather strip, trunk room weather strip, sunroof weather strip, ventilator weather strip and corner strip. As the architectural materials, there may be exemplified gaskets, airtight elements, jointing parts and damper seal at door top. For others, products for

leisure and sports, such as golf club grip, grip of baseball bat, swimming fins and diving goggles; protecting cover for hoses; and cushions.

【 0097 】

Fig. 1 shows the sectional construction of one embodiment of an automobile weather strip in which the foamed laminate based on olefin according to the present invention is employed. The automobile weather strip 1 shown in Fig. 1 is constructed from a thin core plate 2 and two contact seal lugs 3 arranged on the core plate 2 in a form of curved fins so as to provide for a tight contact onto the window glass to establish a contact seal. The contact seal lug 3 is made of the foamed laminate based on olefin according to the present invention prepared by laminating the substrate layer 4 and the skin layer 5, wherein the skin layer 5 is disposed on the side for contacting with the window glass.

【 0098 】

【 INVENTIVE EFFECTS 】

The foamed laminate based on olefin according to the present invention is prepared at a high foaming expansion ratio and provides a soft hand touch and, in addition, it is superior in the appearance, abrasion resistance, durability and sliding performance. The laminate according to the present invention can be produced easily and is easy in the recycled use due to the use of, as the principal raw material, olefinic polymers, providing, thus, a superior economical efficiency.

【 0099 】

**【 MODE FOR EMBODYING THE INVENTION 】**

Below, the present invention is described in more detail by way of Examples, though the present invention is by no means restricted by these Examples. Components used in the subsequent Examples and Comparative Examples are as given below:

**【 0100 】**

- A polyolefin resin (a-11):

A propylene/ethylene block copolymer which has an MFR (ASTM D-1238-65T, 230 °C, 2.16 kg load) of 50 g/10 min., a density of 0.910 cm<sup>3</sup> and an ethylene content of 8 mole %.

- An ethylene/ $\alpha$ -olefin copolymer rubber (a-21):

An ethylene/propylene/5-ethylidene-2-norbornene copolymer rubber which has an ethylene content of 63 mole %, an iodine value of 13 and a Mooney viscosity [ML<sub>1+4</sub>(100 °C)] of 100.

- An oil-extended ethylene/ $\alpha$ -olefin copolymer rubber (a-22):

This is prepared by adding to the ethylenic rubber (a-21) a softening agent (a-31) as given below.

- A softening agent (a-31):

This is a paraffinic process oil (a product of Idemitsu Kosan Co., Ltd. with trademark PW-380).

- An olefinic thermoplastic resin (B-1):

This is a homopolymer of propylene having an MFR (ASTM D-1238-65T, 230 °C, 2.16 kg load) of 0.3 g/10 min. and a density of 0.910 g/cm<sup>3</sup>.

**【 0101 】**

- A foaming agent (C-1):

This is azodicarbonamide.

○ An ultrahigh molecular weight polyolefin composition (Y-1):

An ultrahigh molecular weight polyethylene composition which has an intrinsic viscosity ( $\eta$ ) of 7.0 dl/g as determined in decalin at 135 °C and a density of 0.965 g/cm<sup>3</sup>.

○ A rubber (d-11):

An ethylene/propylene/5-ethylidene-2-norbornene copolymer rubber which has an ethylene content of 70 mole %, an iodine value of 12 and a Mooney viscosity [ML<sub>1+4</sub>(100 °C)] of 120.

○ A polyolefin resin (d-21):

A propylene/ethylene block-copolymer which has an MFR (ASTM D-1238-65T, 230 °C, 2.16 kg load) of 13 g/10 min., a density of 0.91 g/cm<sup>3</sup> and an ethylene content of 3 mole %.

【 0102 】

○ An organopolysiloxane (E-1):

This is a silicone oil {a product of Toray-Dow Corning K.K. with trademark SH200 (3000 cSt)}.

○ An organopolysiloxane (E-2):

This is a silicone oil/polypropylene masterbatch {a product of Toray-Dow Corning K.K. with trademark BY27-002 (having an ultrahigh molecular weight silicone oil content of 50 % by weight)}.

○ A fluorine-containing polymer (F-1):

A product of Sumitomo Three M K.K. with trademark DYNAMER FX-9613 (Content of the fluorine-containing polymer of 90 %).

○ An antistatic agent (G-1):

A product of Kao Corporation with trademark ELECTROSTRIPPER TS-6B.

○ A polyolefin resin (H-1):

A propylene/ethylene block-copolymer which has an MFR (ASTM D-1238-65T, 230 °C, 2.16 kg load) of 13 g/10 min., a density of 0.91 g/cm<sup>3</sup> and an ethylene content of 3 mole %.

【 0103 】

Example 1

(1) Production of an olefinic thermoplastic elastomer (A-1):

On a Bumbury's mixer, 30 parts by weight of the polyolefin resin (a-11) and 70 parts by weight of the ethylene/ $\alpha$ -olefin copolymer rubber (a-21) were kneaded at 180 °C under a nitrogen atmosphere for 5 minutes, followed by passing through a sheeting roll to produce a pelletized product by a sheet cutter. Then, 100 parts by weight of this pelletized product and a solution of 0.3 part by weight of 1,3-bis(tert-butylperoxyisopropyl)benzene dissolved in 0.3 part by weight of divinylbenzene were mixed on a tumbler type blender, in order to coat the pellets with the solution uniformly. Thereafter, the resulting pelletized product was extruded by an extruder at 210 °C under a nitrogen atmosphere to effect the dynamic heat treatment, whereby an olefinic thermoplastic elastomer (A-1) having a gel content of 77 % by weight was obtained.

【 0104 】

## (2) Production of the laminate

There were blended 100 parts by weight of the ethylenic thermoplastic elastomer (A-1), 5 parts by weight of the olefinic thermoplastic resin (B-1) and 5 parts by weight of the foaming agent (C-1) on a tumbler type blender to prepare an olefinic foamable composition. This foamable composition was extrusion-molded at a die temperature of 150 °C to effect a foaming molding to form a core plate and substrate layer portions, while at the same time the ultrahigh molecular weight polyethylene composition (Y-1) was co-extruded to form a skin layer, whereupon the substrate layer and the skin layer were heat melt-bonded to thereby produce a weather strip as shown in Fig. 1. The foaming expansion ratio of the resulting weather strip was 2.2 times the original composition volume.

### 【 0105 】

The so-produced weather strip was assembled on a window frame for testing, whereupon a window glass having a thickness of 3.2 mm was inserted therein, in order to carry out a durability test (repeating test of up-and-down motion of the window glass). The weather strip had withstood 50,000 repetitions of up-and-down motion without suffering from any yielding phenomenon nor abrasion and had maintained its function as weather strip.

### 【 0106 】

## Example 2

In the same manner as in Example 1, an olefinic thermoplastic elastomer (A-2) was obtained using 30

parts by weight of the polyolefin resin (a-11), 70 parts by weight of the ethylene/ $\alpha$ -olefin copolymer rubber (a-21) and 50 parts by weight of the softening agent (a-31). This olefinic thermoplastic elastomer (A-2) had a gel content of 71 % by weight. Then, using the olefinic thermoplastic elastomer (A-2), an olefinic foamable composition was prepared in the same way as in Example 1. Thereafter, a weather strip was produced together with the skin layer same as that of Example 1, for which a durability test was carried out. The test showed that this weather strip had withstood the 50,000 repetition test and maintained its function as weather strip. The foaming expansion ratio of the resulting weather strip was found to be 2.3 times the original composition volume.

【 0107】

### Example 3

In the same manner as in Example 1, except that 120 parts by weight of the oil-extended ethylene/ $\alpha$ -olefin copolymer rubber (a-22) were used instead of using 70 parts by weight of the ethylene/ $\alpha$ -olefin copolymer rubber (a-21), an olefinic thermoplastic elastomer (A-3) was obtained. This olefinic thermoplastic elastomer (A-3) had a gel content of 73 % by weight. Then, using the olefinic thermoplastic elastomer (A-3), an olefinic foamable composition was prepared in the same way as in Example 1, thereafter, a weather strip was produced using together the skin layer same as that of Example 1, for which the durability test was carried out. The test showed that this weather strip had withstood the 50,000

repetition test and maintained its function as weather strip. The foaming expansion ratio of the resulting weather strip was found to be 2.3 times the original composition volume.

【 0108 】

Example 4

Using 30 parts by weight of the polyolefin resin (a-11), 70 parts by weight of an ethylene/ $\alpha$ -olefin copolymer rubber (a-21), 50 parts by weight of the softening agent (a-31) and 30 parts by weight of a butyl rubber (having an unsaturation degree of 0.5 % and an Mooney viscosity  $[ML_{1+4}(100\text{ }^{\circ}\text{C})]$  of 40), an olefinic thermoplastic elastomer (A-4) was obtained in the same procedures as in Example 1. This olefinic thermoplastic elastomer (A-4) had a gel content of 81 % by weight. Then, using the olefinic thermoplastic elastomer (A-4), an olefinic foamable composition was prepared in the same way as in Example 1, thereafter, a weather strip was produced using together the skin layer same as that of Example 1, for which the durability test was carried out. The test showed that this weather strip had withstood the 50,000 repetition test and maintained its function as weather strip. The poaming expansion ratio of the resulting weather strip was found to be 2.6 times the original composition volume.

【 0109 】

Example 5

(1) Production of an olefinic thermoplastic elastomer (D-1):

On a Bumbury's mixer, 60 parts by weight of the



rubber (d-11) and 40 parts by weight of the crystalline polyolefin resin (d-21) were kneaded at 180 °C under a nitrogen atmosphere for 5 minutes, followed by passing through a sheeting roll to produce dice-formed pellets by a sheet cutter. Then, the dice-formed pellets were mixed with 0.2 part by weight of 1,3-bis(tert-butylperoxyisopropyl)benzene and 0.2 part by weight of divinylbenzene on a Henschell mixer. Thereafter, the resulting pelletized product was extruded at 210 °C by a double shaft extruder having an L/D value of 40 and a screw diameter of 50 mm under a nitrogen atmosphere, whereby an olefinic thermoplastic elastomer (D-1) was obtained. The resulting olefinic thermoplastic elastomer (D-1) had a gell content of 78 % by weight, as determined by the method given previously.

【 0110】

(2) Production of the laminate

There were kneaded 100 parts by weight of the olefinic thermoplastic elastomer (D-1) and 2 parts by weight of the organopolysiloxane (E-1) on a double shaft extruder to prepare an olefinic thermoplastic elastomer composition (Z-1) for the skin layer.

This olefinic thermoplastic elastomer composition (Z-1) was molded under co-extrusion together with the olefinic foamable composition same as that of Example 1 to produce a weather strip, for which the durability test was carried out. The weather strip had withstood the 50,000 repetition test and had maintained its function as weather strip.

【 0111】

### Example 6

On a double shaft extruder, 100 parts by weight of the olefinic thermoplastic elastomer (D-1) obtained in Example 5, 2 parts by weight of the organopoly-siloxane (E-1) and 14 parts by weight of the organopolysiloxane (E-2) were kneaded, whereby an olefinic thermoplastic elastomer composition (Z-2) for the skin layer was obtained.

This olefinic thermoplastic elastomer composition (Z-2) was molded under co-extrusion together with the olefinic foamable composition same as that of Example 1 to produce a weather strip, for which the durability test was carried out. The weather strip had withstood the 50,000 repetition test and had maintained its function as weather strip.

【 0112】

### Example 7

On a double shaft extruder, 100 parts by weight of the olefinic thermoplastic elastomer (D-1) obtained in Example 5 and 3 parts by weight of the fluorine-containing polymer (F-1) were kneaded, whereby an olefinic thermoplastic elastomer composition (Z-3) for the skin layer was obtained.

This olefinic thermoplastic elastomer composition (Z-3) was molded under co-extrusion together with the olefinic foamable composition same as that of Example 1 to produce a weather strip, for which the durability test was carried out. The weather strip had withstood the 50,000 repetition test and had maintained its function as weather strip.

## 【 0113 】

## Example 8

On a double shaft extruder, 100 parts by weight of the olefinic thermoplastic elastomer (D-1) obtained in Example 5 and 3 parts by weight of the antistatic agent (G-1) were kneaded, whereby an olefinic thermoplastic elastomer composition (Z-4) for the skin layer was obtained.

This olefinic thermoplastic elastomer composition (Z-4) was molded under co-extrusion together with the olefinic foamable composition same as that of Example 1 to produce a weather strip, for which the durability test was carried out. The weather strip had withstood the 50,000 repetition test and had maintained its function as weather strip.

## 【 0114 】

## Example 9

On a double shaft extruder, 100 parts by weight of the olefinic thermoplastic elastomer (D-1) obtained in Example 5 and 10 parts by weight of the ultrahigh molecular weight polyolefin composition (Y-1) were kneaded, whereby an olefinic thermoplastic elastomer composition (Z-5) for the skin layer was obtained.

This olefinic thermoplastic elastomer composition (Z-5) was molded under co-extrusion together with the olefinic foamable composition same as that of Example 1 to produce a weather strip, for which the durability test was carried out. The weather strip had withstood the 50,000 repetition test and had maintained its function as weather strip.

## 【 0115 】

## Example 10

On a double shaft extruder, 100 parts by weight of the olefinic thermoplastic elastomer (D-1) obtained in Example 5, 100 parts by weight of the ultrahigh molecular weight polyolefin composition (Y-1) and 2 parts by weight of the organopolysiloxane (E-1) were kneaded, whereby an olefinic thermoplastic elastomer composition (Z-6) for the skin layer was obtained.

This olefinic thermoplastic elastomer composition (Z-6) was molded under co-extrusion together with the olefinic foamable composition same as that of Example 1 to produce a weather strip, for which the durability test was carried out. The weather strip had withstood the 50,000 repetition test and had maintained its function as weather strip.

## 【 0116 】

## Example 11

On a double shaft extruder, 100 parts by weight of the olefinic thermoplastic elastomer (D-1) obtained in Example 5, 2 parts by weight of the organopoly-siloxane (E-1) and 30 parts by weight of the polyolefin resin (H-1) were kneaded, whereby an olefinic thermoplastic elastomer composition (Z-7) for the skin layer was obtained.

This olefinic thermoplastic elastomer composition (Z-7) was molded under co-extrusion together with the olefinic foamable composition same as that of Example 1 to produce a weather strip, for which the durability test was carried out. The weather strip had withstood the

50,000 repetition test and had maintained its function as weather strip.

【 0117 】

#### Comparative Example 1

Using a conventional weather strip (having a laminate structure in which a nylon film is attached onto a layer of a soft vinyl chloride resin), the durability test was carried out in the same way as in Example 1. In this test, a breakdown occurred on the face contacting with the window glass after 25,000 repetitions, whereby the friction resistance on the window glass increased considerably to thereby render practical use impossible.

#### 【 BRIEF DESCRIPTION OF THE DRAWINGS 】

##### 【 FIG. 1 】

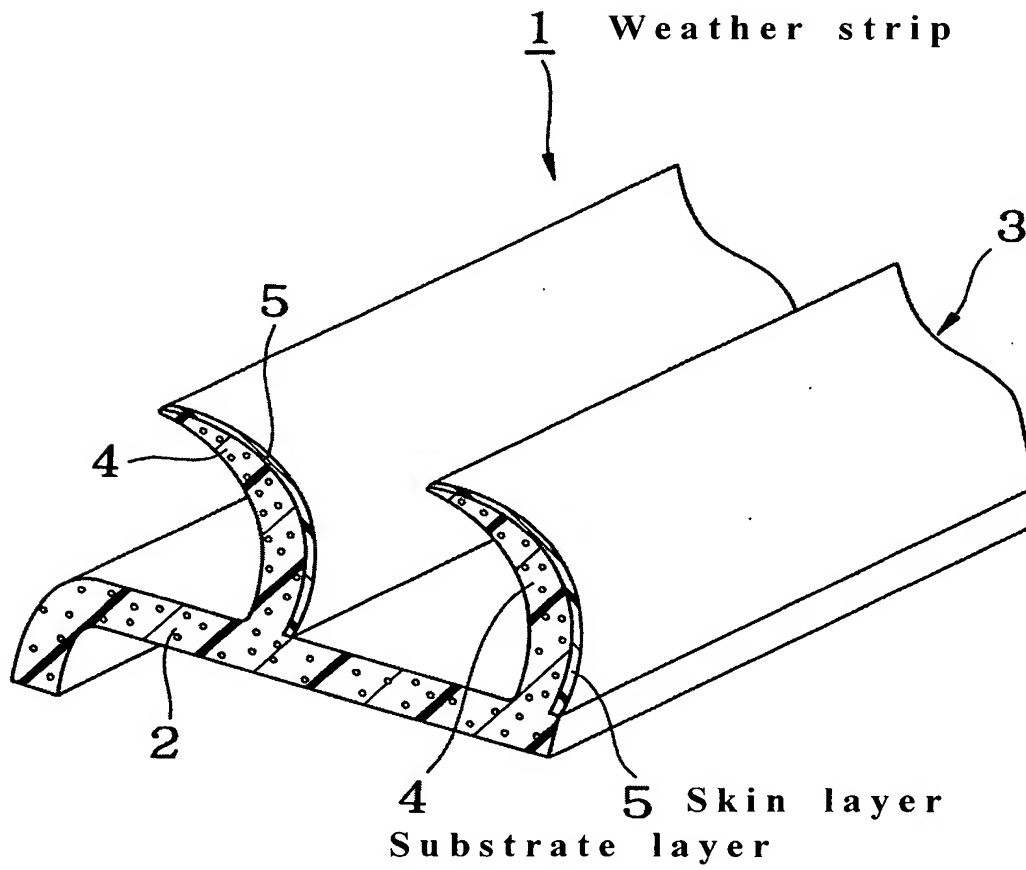
Fig. 1 shows a weather strip comprising the foamed laminate based on olefin according to the present invention in a perspective view, in which a cross section is shown by the front face.

#### 【 EXPLANATION OF SYMBOLS 】

- 1 .... Weather strip
- 2 .... Core plate
- 3 .... Contact seal lug
- 4 .... Substrate layer
- 5 .... Skin layer

【 DESIGNATION OF THE DOCUMENT 】 DRAWINGS

【 FIG. 1 】



【 DESIGNATION OF THE DOCUMENT】      ABSTRACT  
OF THE DISCLOSURE

【 ABSTRACT】

【 PURPOSE】

We provide a foamed laminate based on olefin which is made of an olefinic polymer premitting recycled use and obtainable at a high foaming expansion ratio, exhibits a soft hand touch and which is superior in the appearance, in the resistance to abrasion, in the durability and in the sliding performance.

【 CONSTRUCTION】

A foamed laminate based on olefin in which  
a substrate layer, consisting of a foamed body made of a foamable olefinic composition comprising 100 parts by weight of an olefinic thermoplastic elastomer obtained by subjecting a mixture comprising a polyolefin resin and an ethylene/ $\alpha$ -olefin copolymer rubber resulting to a dynamic heat treatment, 1 - 20 parts by weight of an olefinic thermoplastic resin and a foaming agent, and

a skin layer made of an ultrahigh molecular weight polyolefin resin which has an intrinsic viscosity of 3.5 - 8.3 dl/g or an olefinic thermoplastic elastomer composition which comprises an olefinic thermoplastic elastomer, at least one kind selected from the group consisting of an organopolysiloxane, a fluorine-containing polymer, an antistatic agent, and a polyolefin resin,

are laminated.

【 SELECTED DRAWING】      NONE

INFORMATIONS ON HISTORY OF THE APPLICANT

Identification Number [000005887]

1. Date of Revision 1st October 1997

[Reason of Revision] Change of Name

Address 2-5, Kasumigaseki 3-Chome, Chiyoda-Ku  
Tokyo, Japan

Name MITSUI CHEMICALS, INC.